

Cyclic Bonds in Branched Polymers

Reexamination of the Basic Assumptions of the Gelation Theory through Comparison with the Ilavsky-Dusek Observations

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Abstract

In the theory of gelation it has been implicitly assumed that (I) a cyclic bond is a finite bond that returns to itself; (II) cyclic bonds distribute at random in network structures. In this paper these two assumptions are reexamined from a new point of view. The physical soundness of the assumptions is assessed through comparison with experimental observations.

Key Words: Finiteness of Cyclic Bonds/ Random Distribution of Cyclic Bonds

In developing the theory of branching processes [1, 2, 4–6], we have introduced two basic assumptions: (I) a cyclic bond is a finite link and (II) cyclic bonds distribute randomly in network structures. These two assumptions have served as the basis of the theory of gelation, leading us to the understanding of various phenomena that occur in the gelling processes: upward shift of gel points, existence of critical dilution, and occurrence of permanent sol. In this paper, we reinvestigate the above basic assumptions in order to lay those on firm foundation.

1 Theoretical Background

1.1 On Assumption I

In the theory of branching process, it has been implicitly assumed that a cyclic bond is a finite link, because it returns to the starting point. To date this statement has been accepted as a theorem. However, when analyzed in detail, it is seen that the statement is not necessarily self-evident. To make this issue clearer, an example of a branched structure involving one cyclic bond is illustrated in Fig. 1 for the multiple link system of $f = 3$ and $J = 3$: large filled circles (\bullet) represent monomer units, open circles (\circ) functional units and the symbols (\oslash) junction points. Suppose that a cyclization has occurred to create the bond $1 - b$. Taking a look at this figure, one may raise the objection:

Why can the author affirm that a cyclic bond is finite? It is certain that the bond $1 - b$ emanating from the junction point 1 returns to itself through the route $1 - b - 2 - a - 1$, but at the same time it can extend to infinity, for instance, through the route $1 - b - 3$, doesn't it?

That's right! But the true meaning of the cyclic bond resides in a deeper level. To discuss this problem, it is necessary to keep in mind the following two facts: (A) a cyclic bond gives no effect on the growth of cluster size; it only wastes functional units; (B) once a cyclic bond is formed, the memory of the event of cyclization is completely lost; namely, anyone of 4 bonds ($1 - a$, $a - 2$, $2 - b$ and $b - 1$) can be a cyclic bond.

Because of the fact (A), there must be at least one useless, finite bond that returns to itself. Let it be the bond $1 - b$ as defined above. Then disconnect the bond $1 - b$, as shown in Fig. 1-(B). The situation now becomes apparent. The path from the junction point 1 to 3 is still alive through another route $1 - a - 2 - b - 3$. Whether the bond $1 - b$ is closed or open, the route to the junction point 3 is already constructed through the (intermolecular) bond $1 - a$. It is seen that the cyclic bond is a bond not emanating from the junction point 1, but returning to

itself (see Fig. 1-(C)). When we state that the bond 1-b is a finite bond, it is a cyclic bond, whereas when we state that the bond 1-b can lead to infinity, it is an intermolecular bond. Both the statements are true because of the fact (B). The same argument, of course, applies equally to the other bonds, $1 - a$, $a - 2$ and $2 - b$.

1.2 On Assumption II

As far as we consider individual clusters such as shown in Fig. 1, it is obvious that the validity of Assumption II is confined to the cyclic structure 1-a-2-b-1. Then it might appear that Assumption II can not be extended beyond the local structure, since individual clusters should contain different sizes, different numbers and different types of rings, so the cyclic structures change from clusters to clusters. Now the problem with which we are faced turns out to be much intricate, theoretical treatment appearing harder. However, in most theoretical treatments of branching process, what is required is the mean properties of the system; cases as to require detailed structural informations of individual clusters are rare. In such average pictures [6], every functional unit has an equal chance of cyclization or intermolecular reaction. Thus, taking the above-mentioned fact (B) into consideration, it may be concluded that there is a sufficient reason for us to accept Assumption II, the random distribution of cyclic bonds.

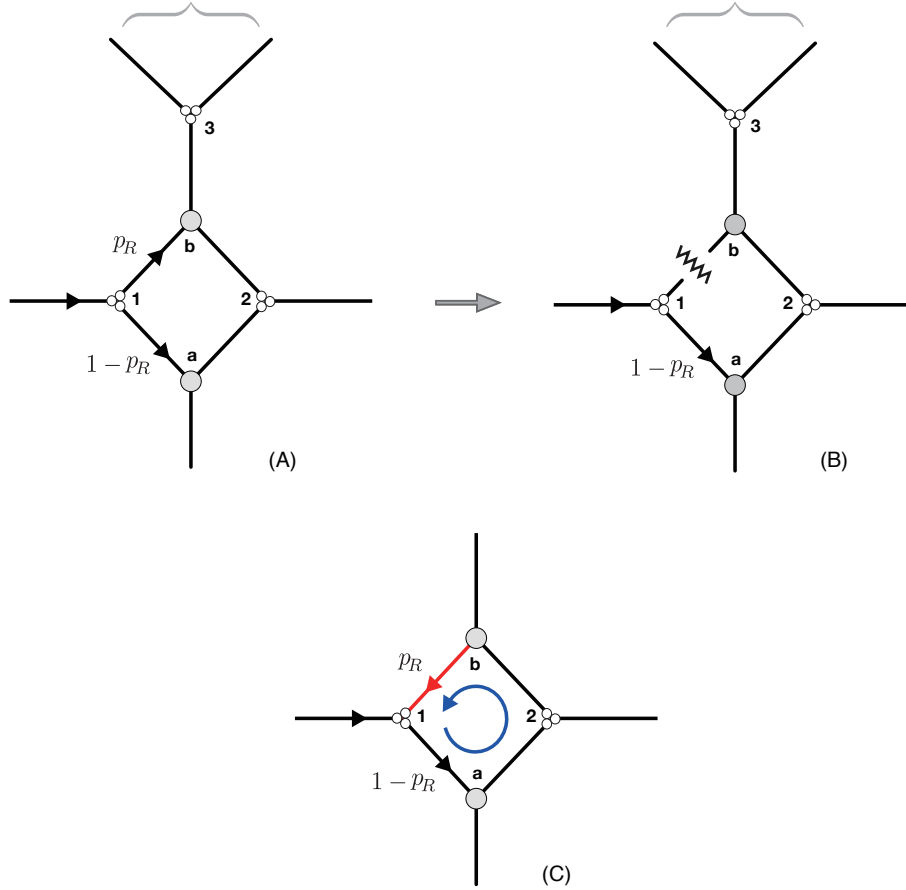


Fig. 1: Representation of a Cyclic Bond in the Multiple Link System of $f = 3$ and $J = 3$.

Our task is then to make a thorough assessment of the validity of Assumptions I and II through comparison with extensive experimental observations.

2 Formulation of Gelling Processes

Consider the branching process in the mixing system of the $R-A_f + R-B_g$ model comprised of various monomers having two different type of functional units, $\{f_i M_{A_i}\}$ and $\{g_j M_{B_j}\}$, where M_{A_i} and M_{B_j} are the numbers of the

A and B type monomers, respectively; f_i and g_j are the corresponding functionalities having positive integers with the subscripts, i and j , signifying $1, 2, 3, \dots$. Chemical bonds can be formed only between A and B functional units. Let $[\Gamma]$ be the total molar concentration of cyclics and V the system volume. Bearing in mind that each ring possesses only one cyclic bond [6], we introduce the notations:

- fraction of cyclic bonds as against A functional units : $p_{R_A} = [\Gamma] / \left(\frac{1}{N_A V} \sum_i f_i M_{A_i} \right) \equiv [\Gamma] / C_f$
- fraction of cyclic bonds as against B functional units : $p_{R_B} = [\Gamma] / \left(\frac{1}{N_A V} \sum_j g_j M_{B_j} \right) \equiv [\Gamma] / C_g$
- fraction of A_i functional units : $\chi_{A_i} = f_i M_{A_i} / \sum_i f_i M_{A_i}$
- fraction of B_j functional units : $\chi_{B_j} = g_j M_{B_j} / \sum_j g_j M_{B_j}$

(1)

2.1 Gel Point

Given Assumptions I and II, the number, α , of branches leading from a given R- A_f unit, via R- B_g units, to the next R- A_f units is simply given by

$$\alpha = \sum_j \chi_{B_j} \sum_{k=0}^{g_j-1} k \binom{g_j-1}{k} p_B^k (1-p_B)^{g_j-1-k} \{1 - P_B(Z|X)\} \times \sum_i \chi_{A_i} \sum_{\ell=0}^{f_i-1} \ell \binom{f_i-1}{\ell} p_A^\ell (1-p_A)^{f_i-1-\ell} \{1 - P_A(Z|X)\} \quad (2)$$

where $P_A(Z|X) = p_{R_A}/p_A$ and $P_B(Z|X) = p_{R_B}/p_B$ represent the conventional conditional probabilities. The critical condition occurs at $\alpha = 1$, so that

$$(p_{A_c} - p_{R_{A_c}})(p_{B_c} - p_{R_{B_c}}) = \frac{1}{(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)} \quad (3)$$

Let $\kappa = \sum_j g_j M_{B_j} / \sum_i f_i M_{A_i}$ be the molar ratio. Then eq. (3) may be recast in the form:

$$p_{A_c} = \sqrt{\frac{\kappa}{(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)}} + \frac{[\Gamma_c]}{C_f} \equiv p_{A_{c0}} + p_{R_{A_c}} \quad (4)$$

which is of the form: $p = p(\text{inter}) + p(\text{ring})$, as expected. Note that the $p(\text{ring})$ term in eq. (4) is the quantity at p_c , so eq. (4) indicates that the gelation occurs at the point where the ratio of the intermolecular bonds to the total number of possible bonds attains the classic gel point with no rings.

To solve eq. (4) we must express $[\Gamma_c]$ as a function of p_{A_c} . It is well-known that the concentration of cyclic species is held constant above the critical initial-monomer-concentration, $C_0 \geq C_0^*$ [6]. For this reason we may regard the following limiting solution of $C_0 \rightarrow \infty$ as the general solution of $[\Gamma]$:

$$[\Gamma] = \sum_{x=1}^{\infty} \varphi_x \frac{[(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)p_A^2/\kappa]^x}{2N_A V x} \quad (\text{for } C_0 \geq C_0^*) \quad (5)$$

Unfortunately, as emphasized previously [6], eq. (5) breaks down for $p_A > p_{A_{c0}}$. So we cannot link directly the limiting solution (5) with eq. (4). To resolve this problem, we expand eq. (5) about $p_A = p_{A_{c0}}$ to obtain

$$[\Gamma(p_A)] \simeq \sum_{x=1}^{\infty} \frac{\varphi_x}{2N_A V x} + \sqrt{\frac{(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)}{\kappa}} \sum_{x=1}^{\infty} \frac{\varphi_x}{N_A V} (p_A - p_{A_{c0}}) \quad (6)$$

In eq. (6), we have made use of the classic relation: $(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)p_{A_{c0}}^2/\kappa = 1$. Let $s = (\langle f_w \rangle - 1)(\langle g_w \rangle - 1)/\kappa$. Then replace p_A in eq. (6) with p_{A_c} and substitute the resulting equation into eq. (4) to yield

$$p_{A_c} = \sqrt{\frac{1}{s}} \left\{ \frac{1 - \frac{\sqrt{s}}{N_A V} \sum_{x=1}^{\infty} \varphi_x \left(1 - \frac{1}{2x}\right) \gamma_f}{1 - \frac{\sqrt{s}}{N_A V} \sum_{x=1}^{\infty} \varphi_x \gamma_f} \right\} \quad (7)$$

where $\gamma_f = 1/C_f$ is the reciprocal of the initial A functional unit concentration. If we define the total functional unit concentration $C_{fg} = \frac{1}{N_{Av}V}(\sum_i f_i M_{A_i} + \sum_j g_j M_{B_j})$ and the total monomer concentration $C = \frac{1}{N_{Av}V}(\sum_i M_{A_i} + \sum_j M_{B_j})$, the following relationship holds between γ_f , $\gamma_{fg} = 1/C_{fg}$ and $\gamma = 1/C$:

$$\gamma_f = (1 + \kappa)\gamma_{fg} = \frac{\langle f_n \rangle \kappa + \langle g_n \rangle}{\langle f_n \rangle \langle g_n \rangle} \gamma \quad (l/mol) \quad (8)$$

where the subscript n denotes the number average quantity.

The condition of the critical dilution can be obtained by imposing the boundary condition, $p_{Ac_0} \leq p_{Ac} \leq 1$, on eq. (7):

$$0 \leq \gamma_f \leq \gamma_{fc} = \frac{1 - 1/\sqrt{s}}{\frac{1}{N_{Av}} \sum_x (-1 + \sqrt{s} + 1/2x) \varphi_x} \quad (9)$$

It is important to notice that eq. (9) is meaningful only if $\kappa \geq 1$, since otherwise the boundary condition, $p_{Ac} = 1$, cannot be fulfilled.

2.2 Post-gelation

Let Q_A be the probability that a chosen branch emanating from the R-A_f monomer unit is finite and Q_B be the corresponding probability for the R-B_g monomer unit. Given Assumptions I and II, one can readily describe a set of the recurrence relations:

$$\begin{aligned} Q_A &= 1 - p_A + p_A \sum_j \chi_{B_j} [P_B(Z|X) + (1 - P_B(Z|X))Q_B^{g_j-1}] \\ Q_B &= 1 - p_B + p_B \sum_i \chi_{A_i} [P_A(Z|X) + (1 - P_A(Z|X))Q_A^{f_i-1}] \end{aligned} \quad (10)$$

The solution other than $Q_A = 1$ or $Q_B = 1$ is

$$p_A p_B (1 - P_A(Z|X))(1 - P_B(Z|X)) \left(\sum_i \chi_{A_i} \sum_{\ell=0}^{f_i-2} Q_A^\ell \right) \left(\sum_j \chi_{B_j} \sum_{m=0}^{g_j-2} Q_B^m \right) = 1 \quad (11)$$

With $P_A(Z|X) = p_{R_A}/p_A$ and $P_B(Z|X) = p_{R_B}/p_B$, and hence $p_{R_A}/p_A \equiv p_{R_B}/p_B$ in mind, substituting $Q_A = Q_B = 1$ into eq. (11), we recover the foregoing critical condition:

$$p_{Ac} = \sqrt{\frac{\kappa}{(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)}} + p_{R_{Ac}} \quad (4')$$

with $\kappa = \sum_j g_j M_{B_j} / \sum_i f_i M_{A_i} \equiv p_A/p_B$ as defined above.

The sol and gel fractions of this system have the forms:

$$\begin{aligned} W_{sol} &= \sum_i w_{A_i} Q_A^{f_i} + \sum_j w_{B_j} Q_B^{g_j} \\ W_{gel} &= 1 - W_{sol} \end{aligned} \quad (12)$$

where w_{A_i} and w_{B_j} represent the weight fraction of the i th A-type monomer unit and that of the j th B-type monomer unit, respectively:

$$\begin{aligned} w_{A_i} &= \frac{m_{A_i} M_{A_i}}{\sum_i m_{A_i} M_{A_i} + \sum_j m_{B_j} M_{B_j}} \\ w_{B_j} &= \frac{m_{B_j} M_{B_j}}{\sum_i m_{A_i} M_{A_i} + \sum_j m_{B_j} M_{B_j}} \end{aligned} \quad (13)$$

and satisfy $\sum_i w_{A_i} + \sum_j w_{B_j} = 1$.

3 Examination of Results

Eqs. (4), (7), (10) and (11) are the direct consequence of Assumptions I and II. In this paper we focus our attention to the post-gelation problem to reexamine the physical soundness of our assumptions through comparison with experiments.

For the assessment of the above theoretical reasonings, we take up the Ilavsky-Dusek observations [1,2] for the gelling process of 4,4'-diphenylmethane diisocyanate (DPMDI) and LHT240 at 55 ~ 60 °C in non-solvent state (see Fig. 2).

Let DPMDI be the R-A_f unit ($f = 2$) and LHT240 the R-B_g unit, respectively, and we have $\kappa = [\text{OH}]/[\text{NCO}]$. LHT240 is prepared from 1,2,6-hexanetriol by means of the anionic polymerization and is considered to be a mixture of diols ($g_1 = 2$) and triols ($g_2 = 3$). Let $x_1 = M_{B_1}/\sum_j M_{B_j}$ be the mole fraction of the diols and $x_2 = M_{B_2}/\sum_j M_{B_j}$ that of the triols to the total amount of alcohols, so that $x_1 + x_2 = 1$. According to the literature [1], the mean functionality is $\langle g_n \rangle = \sum_j g_j x_j = 2.89$. Thus $x_1 = 0.11$ and $x_2 = 0.89$. These give $\langle g_w \rangle = \langle g^2 \rangle / \langle g_n \rangle = 2.92$. Clearly $\{x_j\}$ can be linked with the aforementioned quantities $\{\chi_{B_j}\}$ by the equation:

$$\chi_{B_j} = g_j x_j / \sum_j g_j x_j \quad (14)$$

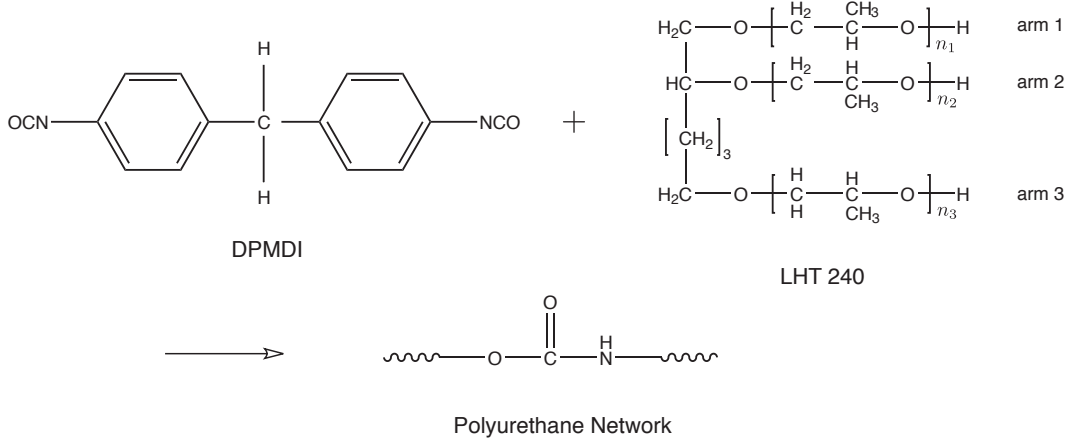


Fig. 2: Formation of polyurethane network by the reaction of DPMDI and LHT240.

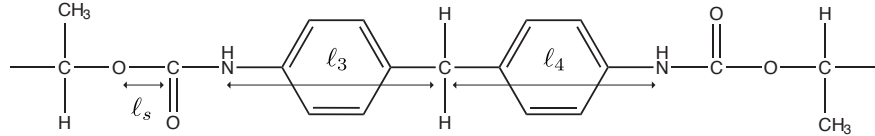


Fig. 3: Backbone structure of the polymer from DPMDI and LHT240.

For the present case, $\chi_{B_1} = 2 \cdot 0.11 / 2.89 = 0.076$ and $\chi_{B_2} = 3 \cdot 0.89 / 2.89 = 0.924$. Solving eqs. (10)-(11) under the condition mentioned above ($f = 2$, $g_1 = 2$, $g_2 = 3$), one has

$$Q_A = 1 + \frac{\kappa \{ \kappa - (1 + \chi_{B_2})(p_A - p_{R_A})^2 \}}{\chi_{B_2}(p_A - p_{R_A})^3} \quad (15)$$

$$Q_B = \frac{\kappa - (p_A - p_{R_A})^2}{\chi_{B_2}(p_A - p_{R_A})^2}$$

together, by eq. (6), with

$$p_{R_A} = \frac{[\Gamma(p_A)]}{C_f} = \left\{ \sum_{x=1}^{\infty} \frac{\varphi_x}{2N_{Av}x} + \sqrt{(\langle f_w \rangle - 1)(\langle g_w \rangle - 1)/\kappa} \sum_{x=1}^{\infty} \frac{\varphi_x}{N_{Av}} (p_A - p_{Ac_0}) \right\} \gamma_f \quad (16)$$

Using the above quantities, the gel fraction can be calculated by the equation

$$W_{gel} = 1 - (w_A Q_A^2 + w_{B_1} Q_B^2 + w_{B_2} Q_B^3) \quad (17)$$

and

$$\begin{aligned} w_A &= \frac{\langle g_n \rangle m_A}{\langle g_n \rangle m_A + f \kappa \langle m_{Bn} \rangle} \\ w_{Bj} &= \frac{f \kappa x_j m_{Bj}}{\langle g_n \rangle m_A + f \kappa \langle m_{Bn} \rangle} \end{aligned} \quad (18)$$

For the diols (m_{B1}) and the triols (m_{B2}) in question, the observed polydispersity index $\langle m_{B,w} \rangle / \langle m_{B,n} \rangle = 1.03$ [3] gives two possible solutions: $(m_{B1}, m_{B2}) = \{(359, 751), (1057, 665)\}$. In this paper we examine the solution, $(m_A, m_{B1}, m_{B2}) = (168, 1057, 665)$.

Before performing our simulation, we must evaluate the relative cyclization frequency φ_x defined by

$$\begin{aligned} \varphi_x &= \left(d/2\pi^{d/2} l_s^d \right) \int_0^{d/2\nu_x} t^{\frac{d}{2}-1} e^{-t} dt \\ \nu_x &= \langle r_x^2 \rangle / l_s^2 = C_F (\xi_e x - 1) \end{aligned} \quad (19)$$

For this purpose, it is necessary to acquire the information about the effective bond number ξ_e within the repeating unit. Set the standard bond length $l_s = 1.36 \text{ \AA}$, and the virtual bonds, $l_3 = l_4 = 5.69 \text{ \AA}$ (see Fig. 3). Then we can calculate the required number for the (i, j) arm pairs as

$$\begin{aligned} \xi_{i,j} &= \frac{1}{1.36^2} \{ 1.36^2 + 1.36^2 + 5.69^2 + 5.69^2 + 1.36^2 + 1.36^2 + (3.3)(1.41^2 + 1.53^2 + 1.41^2) \\ &\quad + 1.41^2 + t \times 1.53^2 + 1.41^2 + (3.3)(1.41^2 + 1.53^2 + 1.41^2) \} \end{aligned} \quad (20)$$

where $t = 1$ for $\xi_{1,2}$, $t = 4$ for $\xi_{2,3}$ and $t = 5$ for $\xi_{1,3}$. And we have

$$\bar{\xi}_e = \frac{1}{3}(\xi_{1,2} + \xi_{2,3} + \xi_{1,3}) = 67.92 \quad (21)$$

so that $\nu_x = \langle r_x^2 \rangle / l_s^2 \simeq C_F (68x - 1)$. We set $C_F = 4.5$, the same value as that for the HMDI-LHT240 system [6]. Now we can evaluate the relative cyclization frequency φ_x under the condition of $d = 3$. The results are summarized in Table 1. Making use of these data, we can plot the weight fraction W_{gel} of gel as a function of the molar ratio $\kappa = [\text{OH}]/[\text{NCO}]$; the result is illustrated in Fig. 4 together with the experimental points by Ilavsky and Dusek [1]; the solid line represents the theoretical line based on eqs. (15)–(19), and the dotted line the prediction by the ideal tree theory without rings ($p_R = 0$). Agreement between the theory and the experiment is very excellent for $\kappa \geq 1$, whereas marked disagreement is observed for the $\kappa \leq 1$ zone. The latter phenomenon may be ascribed to side reactions, under the condition rich in $-\text{NCO}$ moiety, caused by the recombination between urethane bonds $-\text{NH}(\text{CO})\text{O}-$ and unreacted $-\text{NCO}$ functional units to give rise to, for instance, allophanate structures [1]. The results are in good accord with the theoretical calculation based on the cascade theory by Ilavsky and Dusek [1].

It may be concluded that the present results confirm the physical soundness of Assumptions I and II.

Table 1: Physicochemical parameters for DPMDI-LHT240.

parameters	unit	values	
molecular mass	m	DPMDI : $m_A = 250$	LHT240 : $\langle m_{B,n} \rangle = 708$
specific gravity (60 °C)	ρ	DPMDI : $\rho_A \simeq 1.0$	LHT240 : $\rho_B \simeq 1.0$
f		2	
$\langle g_n \rangle$		2.89	
$\langle g_w \rangle$		2.92	
C_F		4.5	
ξ_e		68	
l_s	(Å)	1.36	
cyclization frequency			
$\sum_{x=1}^{\infty} \varphi_x \frac{1}{N_{Av}}$	(mol/l)	0.108	
$\sum_{x=1}^{\infty} \varphi_x \frac{1}{2N_{Av}x}$	(mol/l)	0.028	

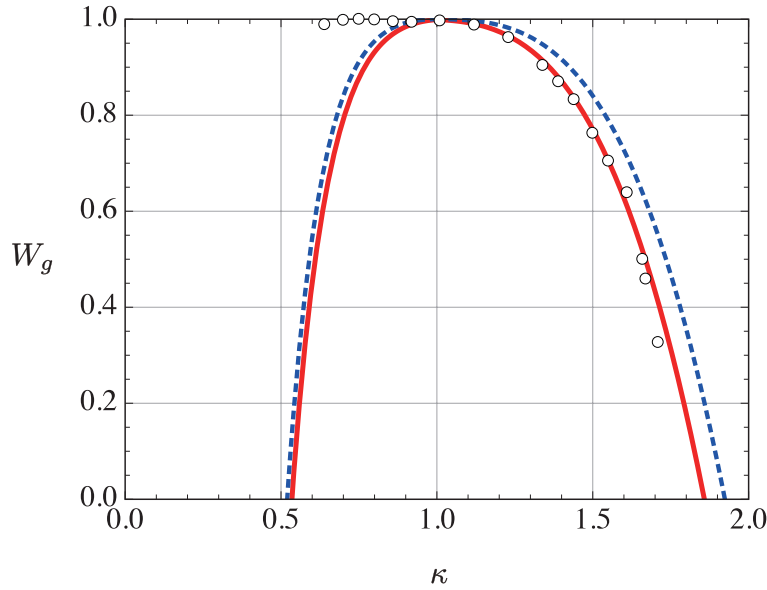


Fig. 4: Gel fraction as against $\kappa = [\text{OH}]/[\text{NCO}]$. Solid line (—): theoretical line by eqs. (15)–(19); dotted line (···): prediction by the ideal tree theory with no rings ($p_R = 0$); (○): experimental points by Ilavsky and Dusek [1].

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